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Summary

Large inputs of woody debris to soil can improve the soil. We examined the fate of woody debris buried in soil after fire-free forest conversion to cropland in French Guiana. We measured the mass loss of woody debris > 4 mm on five sampling dates for 4 years after deforestation. Composition of the organic matter of woody debris was analysed with Rock-Eval pyrolysis, which enabled us to distinguish a labile carbon pool (C_{lab}) and a resistant carbon pool (C_{res}). Decomposition of woody debris followed a first-order function with a half-life of 17.6 months. During the decomposition of woody debris > 4 mm, the C:N ratio, hydrogen index (HI) and pyrolysed carbon below 400°C (R400) decreased, suggesting that decarboxylation and dehydrogenation of woody debris occurred. Both C_{lab} and C_{res} stocks decreased with time, but the decrease in C_{lab} was faster. There was little humification of the debris and no long-term biogeochemical preservation of a woody debris fraction, which accords with the first-order decay observed. We conclude that the benefits of ligno-cellulosic inputs for soil organic carbon contents in a tropical humid climate occur during the first year following deforestation.

Résumé

Les apports massifs de débris de bois au sol peuvent améliorer le sol. Nous avons examiné sur un site en Guyane le devenir de débris de bois enfouis dans le sol, suite à la conversion sans brûlis de forêt en cultures. Nous avons mesuré le stock des débris de bois > 4 mm jusqu'à 4 années après déforestation. Les transformations de la matière organique des débris ont bois ont été analysées par la pyrolyse Rock-Eval, nous permettant de distinguer un compartiment de carbone labile (C_{lab}) et un compartiment de carbone résistant (C_{res}) dans ces débris. La décomposition des débris de bois suit une décroissance exponentielle de premier ordre, avec une demi-vie de 17,6 mois. Durant la décomposition des débris, le rapport C/N, l'indice d'hydrogène (HI) et le carbone pyrolysé avant 400°C (R400) diminuent, suggérant des processus de décarboxylation et déshydrogénation qui se mettent en place rapidement après l'enfouissement des débris. Les stocks de C_{lab} et C_{res} diminuent tous deux au cours du temps, avec une cinétique plus rapide pour C_{lab}. Ces résultats indiquent une faible polymérisation de la matière organique des débris, et une absence de préservation biogéochimique d'une partie des débris, en accord avec la décroissance exponentielle observée. Cette étude suggère que les bénéfices des amendements ligno-cellulosiques pour la matière organique des sols sont de courte durée en milieu tropical humide.

Introduction

Organic matter turnover in soil has received much attention for decades because it is the most important terrestrial reservoir of organic carbon (Jobbágy & Jackson, 2000). Decomposition of organic matter releases nutrients for plants and plays an important role in the behaviour of carbon stored in the soil (Powlson *et al.*, 2011). In humid tropical conditions, temperatures and large amounts of rain, in addition to leaching where the soil is porous, lead to degradation and rapid mineralization of organic matter. Indeed, in the forest soil of Amazonia, decomposition of organic matter inputs produces low-molecular-weight compounds, which are leached rapidly or redistributed laterally in the soil (Cerri & Volkoff, 1987).

Human activities (deforestation, fires and intensive cultivation) can affect the soil carbon dynamics of Amazonian ecosystems (Fujisaki *et al.*, 2015). Deforestation in Amazonia results in general

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from the burning of biomass, but fire-free alternatives have been developed to reduce environmental damage from deforestation. These fire-free systems produce large amounts of woody residues from the shredding of vegetation. Woody residues reduce soil erosivity and improve short-term physical and chemical properties of soil. The increase in soil bulk density is less than with slash-and-burn methods (Comte *et al.*, 2012; Perrin *et al.*, 2014), and concentrations of plant nutrients increase (Comte *et al.*, 2012). Nevertheless, the mass of woody debris could decrease quickly and its benefits might be short lived. Davidson *et al.* (2008) reported that the carbon stock from the litter layer decreased dramatically in less than 2 years in a chop-and-mulch system. Soil amendment with ramial wood chips leads, in general, to an increase in soil organic matter content (Barthès *et al.*, 2010); however, to our knowledge specific studies on the decomposition of woody debris in soil and its contribution to the soil carbon stock are still lacking for a humid tropical climate.

When plant debris is incorporated into soil, leaching, mineralization and biological and biochemical fragmentation can occur (Swift *et al.*, 1979). In parallel with these mechanisms of decomposition, parts of the plant structures might be humified; macromolecules are synthesized by condensation reactions, and nitrogen enrichment occurs (Andreux & Meunier-Lamy, 1994).

Classical approaches for qualitative studies of litter humification are based on a broad spectrum of physico-chemical acid and or alkaline extractions (Pansu & Gautheyrou, 2006). However, considering the processes involved in the decomposition sequence, and in particular the alteration of the molecules, their microbial, enzymatic or abiotic neoformation all occur at the same time (Andreux & Meunier-Lamy, 1994; Almendros, 2008). Therefore, extractive techniques are not always appropriate and new approaches may have to be developed using the methods of organic geochemistry. Rock-Eval pyrolysis was developed initially to study hydrocarbons and kerogen from sedimentary rocks (Espitalié *et al.*, 1985). Recently, it has been shown that Rock-Eval pyrolysis could provide valuable information about the organic matter composition of soil and sediments (Disnar *et al.*, 2003; Delarue *et al.*, 2011; Carrie *et al.*, 2012; Saenger *et al.*, 2013). Rock-Eval pyrolysis does not require sample pretreatment as for pyrolysis GC-MS, and it includes a stage where organic matter is pyrolysed in an inert atmosphere, whereas thermogravimetric analysis with differential scanning calorimetry (TG-DSC) is done in an oxygenated atmosphere.

We aim to define the decomposition kinetics and geochemistry of woody debris buried in soil over time in the context of fire-free forest clearance in Amazonia by mass loss assessment coupled with Rock-Eval pyrolysis. We hypothesize that given the biogeochemical nature of woody debris in tropical humid forests, much of that produced during forest clearance could be preserved or humified and might lead to carbon storage in soil. We also evaluated Rock-Eval pyrolysis to assess the decomposition of organic matter over time.

Materials and methods

Study site

The experimental site is in French Guiana (5°17′55″N/52°55′01″W). The climate is wet humid tropical (Ami type in Köppen–Geiger classification). The mean annual temperature is 27.3°C and mean annual precipitation is 2770 mm, with a dry season from mid-August to mid-November. The soil is a 'ferralitisol meuble kaolinitique jaune' (AFES, 2009) or Hyperferralic Ferralsol (IUSS Working Group, 2007) with a sandy-clay texture and a porosity that favours vertical drainage. The main soil characteristics to 30-cm depth are summarized in Table 1.

Native forest was cleared over an area of 2 ha in October 2008. Trunks and stems of diameter less than 15 cm (corresponding to the undergrowth) were chopped with a vertical axis mulcher with chains mounted on a 20-t wheeled excavator that produced woody debris between 10 and 30 cm in length. The resulting chopped biomass represents about 3–13% of the total standing biomass (Perrin *et al.*, 2014). Timber and larger trunks were removed and stacked outside the study area. In December–January 2009, the soil was limed (1 t ha^{-1} of crushed limestone and 0.45 t ha^{-1} of powdered dolomite), tilled with a disk harrow to 20-cm depth and cover crops were sown (a mixture of grass and legumes). In October 2009, large woody debris and cover crop residues were chopped to a maximum length of 5–7 cm with a forestry mulcher mounted on a self-propelled wheeled machine (Plaisance VT300, Montigny, France), and incorporated into the soil to about 10-cm depth. The soil was then cultivated to grow grass and annual crops, which were planted in December 2009. Three crop systems were established:

Table 1 Physical and chemical properties of the soil's surface layer before forest clearing at the Combi site

		Particle size										
		Sand	Silt	Clay							C	N
Depth / cm	Gravels / % bulk soil	/ %			Bulk density / g cm^{-3}	Porosity	pH in H_2O	Al^{+++} / mol_c kg^{-1}	CEC / mol_c kg^{-1}	V / %	/ g kg^{-1}	
0–5	7.7	75.3	3.0	21.8	1.0	0.6	4.3	1.0	8.6	19.1	26.8	1.6
5–10	7.0	71.6	3.3	25.1	1.3	0.5	4.3	1.2	6.6	9.5	18.1	1.1
10–20	8.3	68.2	3.4	28.4	1.4	0.5	4.3	1.0	5.7	7.4	14.3	0.9
20–30	11.9	63.9	3.8	32.3	1.5	0.4	4.4	0.8	4.0	6.7	8.8	0.6

For pH measurement, soil:water ratio = 1:2.5.
CEC = cation exchange capacity; V = base saturation.
Modified from Perrin *et al.* (2014).

Table 2 Number of samples analysed

Date	Number of quadrats or soil samples collected	Number of woody debris samples analysed with Rock-Eval and chemical methods
October 2008	14	12
November 2009	18	6
April 2010	18	6
November 2010	72	6
November 2011	72	6
November 2012	72	6

Mass loss of woody debris was assessed with quadrats and from the soil samples collected. Woody debris samples analysed with Rock-Eval and chemical methods were selected randomly from the whole set of woody debris available at each date.

(i) grassland that was mowed twice a year, (ii) rotation of maize and soya beans with no tillage and (iii) rotation of maize and soya beans with disk tillage to 15-cm depth. In the three systems, the soil was limed once a year in November with powdered dolomite (1 t ha^{-1}). Four replicate plots (10 m × 20 m) were set up for each system in a randomized complete block design. The complete management history is given in Perrin *et al.* (2014).

Woody debris sampling and sorting

Woody debris was sampled immediately after deforestation in October 2008 in 14 quadrats of 0.68 m^2 area that were placed randomly in the deforested area. After establishment of the cropland, the woody debris that remained in the soil samples was separated from the mineral soil. The soil was sampled on five dates after crop harvests and before lime application: November 2009 ($n = 18$ sampling points), April 2010 ($n = 18$), November 2010 ($n = 72$), November 2011 ($n = 72$) and November 2012 ($n = 72$) (Table 2). In November 2009 and April 2010 only three plots (one replicate block) were sampled, with six sampling points per plot, resulting in 18 sampling points. Given the considerable spatial variation in the distribution of woody debris, four blocks were sampled from November 2010. Soil cores (0.08-m diameter) were taken with a manual auger from four depths: 0–5, 5–10, 10–20 and 20–30 cm. From these soil cores, we determined the bulk density and the woody debris mass. Bulk density was calculated for all sampling dates, with the weight of each soil core corrected for soil moisture determined on a subsample dried at 105°C for 48 hours. Soil samples were air-dried and sieved at 2 mm. Plant fragments > 2 mm were dried at 60°C for 72 hours and sieved at 4 mm. Woody debris was sorted manually on the 4-mm sieve and weighed. The amount of woody debris, *S*, > 4 mm for each sample was calculated as:

$$S = W \times E \times D_b, \quad (1)$$

where *S* is the stock of woody debris in t ha^{-1}, *W* is the woody debris content in the layer, *E* is the thickness of the layer and D_b its bulk density. For each sampling point, the values of *S* for each of the four layers were summed to obtain the stock of woody debris in the 0–30 cm layer.

Chemical analysis

Carbon and nitrogen contents were measured on samples of woody debris. For October 2008, 12 samples were selected randomly from the 14 quadrats. For the next five sampling dates, six samples of woody debris were selected randomly for each date from the woody debris sorted into soil samples, which integrated the whole 0–30-cm soil layer for each selected point (Table 2). Woody debris samples were crushed finely prior to analysis, and their moisture content was measured by oven-drying at 105°C for 48 hours. Elementary analysis by dry combustion (Thermoquest NA 2100) gave total carbon (C_{dc}) and nitrogen contents and the C:N ratio of the woody debris samples. For the 12 samples from October 2008, three replicates were analysed to assess the variability of aliquot samples. Standard errors for these samples did not exceed 8 g C kg^{-1}. We calculated the carbon stock of woody debris in soil to 30-cm depth from C_{dc} and biomass stock.

As woody debris was separated from soil samples, it could include small mineral soil particles. Therefore, we determined organic matter contents (OM) by 2 hours loss-on-ignition in an oven to 700°C, and we could express results in units of organic compounds per unit of pure organic matter.

Rock-Eval analysis

The bulk composition of woody debris was determined by Rock-Eval (RE) pyrolysis on the same crushed samples that underwent chemical analyses (Table 2). Sample mass was about 50 mg. We used an RE6 pyrolyser (turbo model, Vinci Technologies®, Nanterre, France). Rock-Eval pyrolysis has two steps: first, samples are pyrolysed in an inert N_2 atmosphere (pyrolysis stage) at 200 to 650°C, and a flame ionization detector (FID) and infrared (IR) cells detect compounds released by thermal decomposition of the organic matter. Second, the residual material is burned in an oxidation oven (oxidation stage) at 450–750°C, and IR cells detect the oxygenated compounds released. For both stages the heating rate is 30°C $minute^{-1}$. Five pyrograms are produced during Rock-Eval pyrolysis related to the release of hydrocarbons (HC) (S1 and S2 pyrograms) and CO and CO_2 (S3 pyrogram) during the pyrolysis stage, and CO and CO_2 (S4 and S5 pyrograms) are released during the oxidation stage. The indices HI (hydrogen index) and OI (oxygen index) are calculated from S2 and S3 pyrograms (pyrolysis stage), respectively. The HI is correlated with the H:C ratio of the material, and OI is correlated with the O:C ratio of the material. Total organic carbon (TOC) represents the sum of the carbon signal obtained from pyrolysis and oxidation. More information about the apparatus and Rock-Eval pyrolysis methodology is given in Espitalié *et al.* (1985), Lafargue *et al.* (1998) and Behar *et al.* (2001). The different values derived from the Rock-Eval pyrolysis are commonly called 'parameters' in the literature; however, in this paper we use the term 'variables'.

Table 3 Variables calculated from Rock-Eval pyrolysis (adapted from Behar *et al.*, 2001), and recalculated carbon fractions in woody debris

Variable	Detector - oven	Unit	Equations	Name
Rock-Eval variables				
HI	FID[a]–pyrolysis	mg HC g^{-1} TOC	$S2 \times 100/TOC$	Hydrogen index
OI	IR[b]–pyrolysis	mg CO_2 g^{-1} TOC	$S3 \times 100/TOC$	Oxygen index
R400	FID–pyrolysis	–	S2 peak area below 400°C / total S2 peak area	R400
PC	FID & IR–pyrolysis	g kg^{-1} sample	$\left[[(S1+S2)\times 0.83]+\left[S3\times\frac{12}{44}\right]+\left[\left(S3CO+\frac{S3'CO}{2}\right)\times\frac{12}{28}\right]\right]/10$	Pyrolysable organic carbon
RC	IR–oxidation	g kg^{-1} sample	$\left[\left[S4CO\times\frac{12}{28}\right]+\left[S4CO_2\times\frac{12}{44}\right]\right]/10$	Residual organic carbon
MinC	IR–pyrolysis & oxidation	g kg^{-1} sample	$\left[\left[S3'\times\frac{12}{44}\right]+\left[\frac{S3'CO}{2}\times\frac{12}{28}\right]+\left[S5\times\frac{12}{44}\right]\right]/10$	Mineral carbon
TOC	–	g kg^{-1} sample	PC + RC + MinC	Total organic carbon
Recalculated carbon fractions				
C_{res}		g kg^{-1} sample	RC + MinC	Resistant carbon
C_{lab}		g kg^{-1} sample	$C_{dc} - C_{res}$	Labile carbon
$C_{lab} : C_{dc}$		–	C_{lab} / C_{dc}	Labile carbon ratio
OM-C_{res}		g kg^{-1} OM	$C_{res} \times OM$[c]	Resistant carbon of the woody debris organic matter
OM-C_{lab}		g kg^{-1} OM	$C_{lab} \times OM$	Labile carbon of the woody debris organic matter
C_{res} stock		t ha^{-1}	$C_{res} \times$ woody debris stock	Stock of resistant carbon in woody debris
C_{lab} stock		t ha^{-1}	$C_{lab} \times$ woody debris stock	Stock of labile carbon in woody debris

[a]Flame ionization detector.
[b]Infrared.
[c]Organic matter (OM) content of woody debris, measured by loss on ignition.
Components recorded during pyrolysis stage: S1, free hydrocarbons; S2, hydrocarbons; S3, organic CO_2; S3′, mineral CO_2; S3CO, organic CO; S3′CO, organic and mineral CO.
Components recorded during oxidation stage: S4CO_2, organic CO_2; S4CO, organic CO; S5, mineral CO_2.

Table 3 summarizes the variables obtained from pyrolysis and the carbon fractions determined from it. Here, we used six variables from the pyrolysis that express the degree of transformation and humification of organic matter (Disnar *et al.*, 2003): (i) HI (hydrogen index); (ii) OI (oxygen index); (iii) R400, the portion of the S2 signal below 400°C; (iv) pyrolysable carbon (PC), the amount of organic carbon released during the pyrolysis stage; (v) residual organic carbon (RC), the amount of organic carbon released during the oxidation stage and (vi) mineral carbon (MinC), the amount of carbon released at the end of pyrolysis and oxidation.

We assumed that the soil and woody debris contained no free carbonate although the soil was limed. The amount of inorganic carbon added by liming did not exceed 0.60 t ha^{-1} between October 2008 and November 2011, whereas the organic carbon stock was 61.2 t ha^{-1} at 0–30-cm depth under forest (Perrin *et al.*, 2014). Liming increased the soil's pH, but it remained acid for 3 years after cultivation; it was less than 5.6 at 0–5-cm depth (Figure 1). The powdered dolomite applied was readily dissolved in the soil. We therefore disregarded inorganic carbon, and assumed that all the carbon compounds from RE analysis had an organic origin, including MinC. Woody debris contained small contents of MinC, ranging from 0.60 to 2.17%, with a similar magnitude of plant and litter samples to that reported by Volland-Tuduri (2005) in the Cerrados (Brazil).

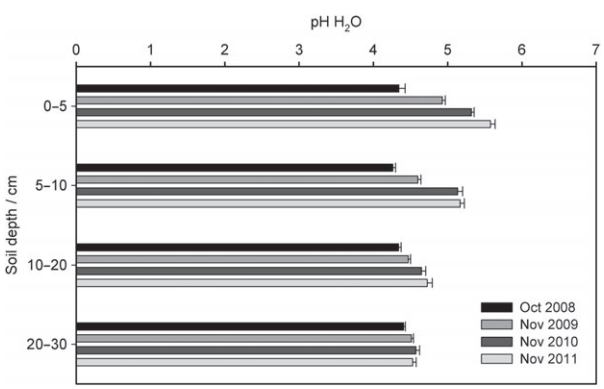

Figure 1 Soil pH in forest soil (October 2008) and after cultivation (without taking account of the cropping system). Error bars represent standard errors ($n = 17$ for October 2008, $n = 72$ for November 2009, $n = 12$ for November 2010 and November 2011). Soil : water ratio = 1:2.5.

From the RE pyrolysis we determined: (i) a resistant carbon pool as $C_{res} = RC + MinC$ and (ii) a labile carbon pool as $C_{lab} = C_{dc} - C_{res}$. In RE pyrolysis, the response of the FID detector

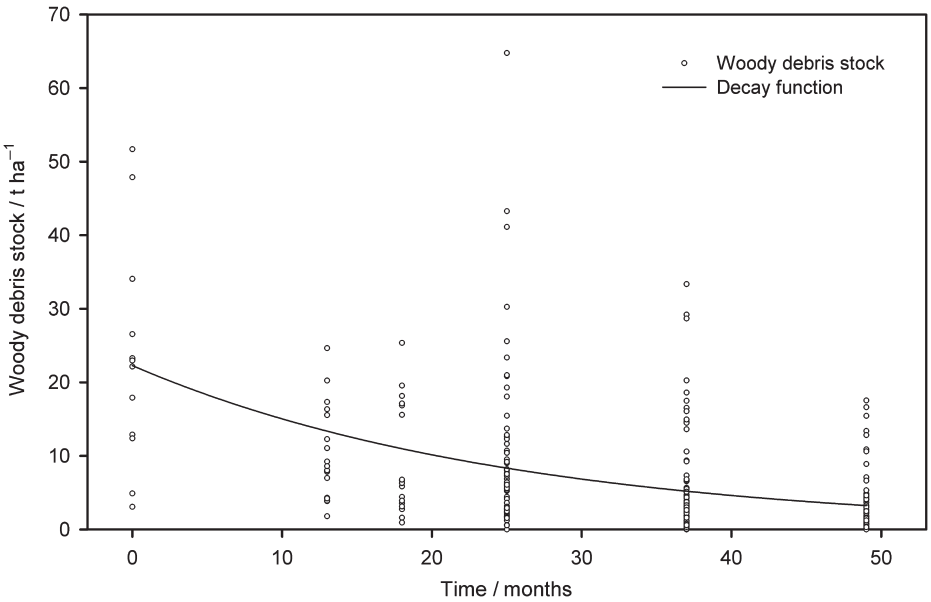

Figure 2 Estimated stock of woody debris > 4 mm plotted against time at 0–30-cm depth in the soil profile in t ha^{-1}. The decay model is $y = 22.3 \times e^{(-0.039t)}$.

during the pyrolysis stage (corresponding to the S2 pyrogram and considered as part of the pyrolysable carbon) is small for cellulose and polysaccharides, which explains why C_{dc} (carbon contents determined by dry combustion) are larger than TOC contents, especially for plant materials and litter horizons (Disnar *et al.*, 2003). We must assume therefore, that pyrolysable carbon (PC) content is underestimated. We attributed this difference in carbon between C_{dc} and TOC to the labile carbon pool. We also determined OM-C_{lab} and OM-C_{res} by relating C_{lab} and C_{res} to the OM content of woody debris.

Statistical analysis

We fitted a non-linear curve to the woody debris stock for the 4 years after deforestation to represent the decay process. We analysed the full dataset without taking into account the blocks and the crop systems because they had no significant effect ($P < 0.05$) on the woody debris stock over time (comparison of the mean for each sampling date with the Kruskal–Wallis test, data not shown). For Rock-Eval variables determined on woody debris (Table 3), means were compared for different sampling dates with the analysis of variance (ANOVA). The null hypothesis tested was that there was no difference between the means of each variable for the six sampling dates. We checked the normality and homoscedasticity of residuals for each ANOVA. None of the variables was transformed. Statistical analysis was done with R version 2.15.2.

Results

Mass loss of woody debris

Woody debris remaining on the soil after deforestation in October 2008, considered to be > 4 mm, was estimated as 24.1 ± 3.8 t ha^{-1}. After deforestation, the stock of woody debris > 4 mm decreased quickly to a final estimate of 3.1 ± 0.5 t ha^{-1} in November 2012 (Figure 2 and Table 4). The mass loss followed an exponential decay of the form:

$$y = 22.3 \times e^{-0.039t}, \quad (2)$$

where y is the woody debris stock in t ha^{-1} and t is the time in months since deforestation. The half-life of woody debris > 4 mm was 17.6 months. Mean residence time (MRT) of woody debris was 25.5 months. The woody debris biomass was still heterogeneous after 25 months (November 2010), but the sample size ($n = 72$) explains the smaller standard error compared with those for November 2009 and April 2010 (Table 4).

Carbon, nitrogen and organic matter content in woody debris

The carbon content of the woody debris decreased with time (Table 4). The carbon stock of the woody debris followed the same trend as the biomass loss, with 11.2 ± 1.9 t ha^{-1} in October 2008 and 1.2 ± 0.2 t ha^{-1} in November 2012. The C:N ratio was 108.5 ± 8.9 at the beginning of the experiment; it decreased to 39.0 ± 4.2 in November 2009 and then stabilized. The organic matter content of woody debris (measured by loss on ignition) was 938 ± 16 g kg^{-1} in October 2008 and decreased to 778 ± 17 g kg^{-1} 3 years after deforestation.

Organic matter composition assessed by Rock-Eval pyrolysis

Characterization of organic matter in woody debris samples by Rock-Eval pyrolysis gave the following results:

1. The hydrogen index (HI) decreased significantly ($F = 18.04$, $P < 0.0001$, Table 5) from October 2008 (486 ± 4 mg HC g^{-1} TOC)

Table 4 Biomass, carbon content and stocks, organic matter (OM), Rock-Eval variables and recalculated carbon fractions of woody debris over time

	Conventional OM properties					Values and carbon fractions from Rock-Eval pyrolysis						
Time	Biomass / t ha^{-1}	C_{dc} / g kg^{-1}	C stock / t ha^{-1}	C:N	OM / g kg^{-1}	HI / mg HC g^{-1} TOC	OI / mg CO_2 g^{-1} TOC	R400	TOC / g kg^{-1}	OM-C_{lab} / g kg^{-1} OM	OM-C_{res} / g kg^{-1} OM	Clab: C_{dc}
October 2008	24.1	465	11.2	108.5	938	486	182	0.76	370	296	201	0.60
0 months	(3.8)	(6)	(1.9)	(8.9)	(16)	(4)	(2)	(0.01)	(7)	(4)	(3)	(0.01)
November 2009	10.2	438	4.5	39.0	877	389	178	0.66	375	241	258	0.48
13 months	(1.5)	(10)	(0.8)	(4.2)	(20)	(33)	(5)	(0.02)	(9)	(14)	(16)	(0.03)
April 2010	9.2	429	3.9	42.1	849	398	167	0.70	373	245	261	0.49
18 months	(1.8)	(16)	(0.9)	(3.3)	(26)	(17)	(10)	(0.04)	(17)	(9)	(14)	(0.02)
November 2010	8.9	430	3.8	45.2	869	388	179	0.72	369	240	254	0.49
25 months	(1.3)	(16)	(0.7)	(4.7)	(26)	(17)	(10)	(0.01)	(13)	(8)	(5)	(0.01)
November 2011	5.9	387	2.3	35.0	778	337	180	0.66	338	218	280	0.44
37 months	(0.8)	(10)	(0.4)	(1.9)	(17)	(14)	(5)	(0.01)	(11)	(7)	(9)	(0.02)
November 2012	3.1	385	1.2	32.4	801	328	200	0.66	341	205	276	0.43
45 months	(0.5)	(7)	(0.2)	(3.1)	(15)	(12)	(14)	(0.02)	(7)	(7)	(5)	(0.01)

Values are means followed in parentheses by standard errors. Biomass and carbon stock were measured from woody debris sorted into soil samples ($n = 14$ in October 2008, $n = 18$ in November 2009 and April 2010, $n = 72$ in November 2010, November 2011 and November 2012). Chemical and Rock-Eval values were measured on woody samples selected randomly from the whole set of woody debris available at each date ($n = 12$ in October 2008 and $n = 6$ for other sampling dates).

Table 5 Results of the ANOVA to test the effect of sampling date of woody debris on the Rock-Eval variables

Variable	Source	Degrees of freedom	Sum of squares	Mean square	F-value	*P*-value
HI	Dates	5	146 074	29 215	18.04	< 0.0001
	Residuals	36	58 312	1 620		
OI	Dates	5	3 585	716.9	1.81	0.1350
	Residuals	36	14 232	395.3		
R400	Dates	5	0.0786	0.0157	6.56	0.0002
	Residuals	36	0.0863	0.0024		
TOC	Dates	5	87.67	17.54	2.28	0.0669
	Residuals	36	276.7	7.68		
OM-Clab	Dates	5	447.3	89.46	21.65	< 0.0001
	Residuals	36	148.7	4.13		
OM-Cres	Dates	5	394.1	78.82	15.31	< 0.0001
	Residuals	36	185.3	5.15		
Clab:Cdc	Dates	5	0.1674	0.0335	20.09	< 0.0001
	Residuals	36	0.0560	0.0017		

See Table 2 for the number of samples.

to November 2012 (328 ± 12 mg HC g^{-1} TOC) (Table 4). The value of R400 also decreased from 0.75 ± 0.01 to 0.66 ± 0.02 one year after deforestation, but it did not change from November 2009 to November 2012 (Table 4). The decrease in R400 after deforestation is due to the decrease in S2 signal intensity before 400°C, rather than an increase in S2 after 400°C in decomposed woody debris (Figure 3).

2. The oxygen index (OI) did not change significantly with time ($F = 1.813$, $P = 0.135$, Table 5); it ranged from 167 ± 10 mg CO_2 g^{-1} TOC in April 2010 to 200 ± 14 mg CO_2 g^{-1} TOC in November 2012 (Table 4).

   The total organic carbon (TOC) contents of woody debris measured by RE pyrolysis did not change significantly ($F = 2.282$, $P = 0.0669$, Table 5), with values from 338 ± 11 g kg^{-1} in November 2011 to 375 ± 9 g kg^{-1} in November 2009 (Table 4).

   The TOC contents were less than the carbon contents measured by dry combustion (C_{dc}). Linear regression between TOC and C_{dc} gave:

$$C_{dc} = 9.8 + 0.62 \times TOC, \quad (3)$$

   with $R^2 = 0.69$ ($P < 0.0001$).

3. Labile carbon in the organic matter of woody debris (OM-C_{lab}) was 296 ± 4 g kg^{-1} in October 2008, and decreased significantly with time ($F = 21.65$, $P < 0.0001$, Table 5) to 205 ± 7 g kg^{-1} in November 2012 (Table 4). On the other hand, resistant carbon in organic matter (OM-C_{res}) increased significantly ($F = 15.31$, $P < 0.0001$, Table 5) after deforestation from 201 ± 3 g kg^{-1} in October 2008 to more than 250 g kg^{-1} after November 2009.

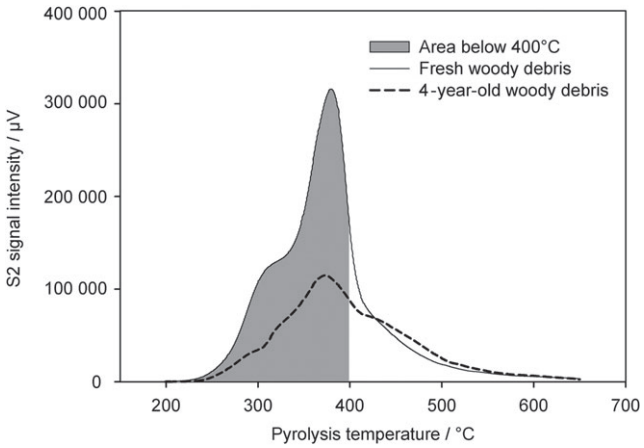

Figure 3 The S2 pyrogram of Rock-Eval pyrolysis for fresh woody debris and for a 4-year-old woody debris sample. R400 is the ratio between area below 400°C and total area.

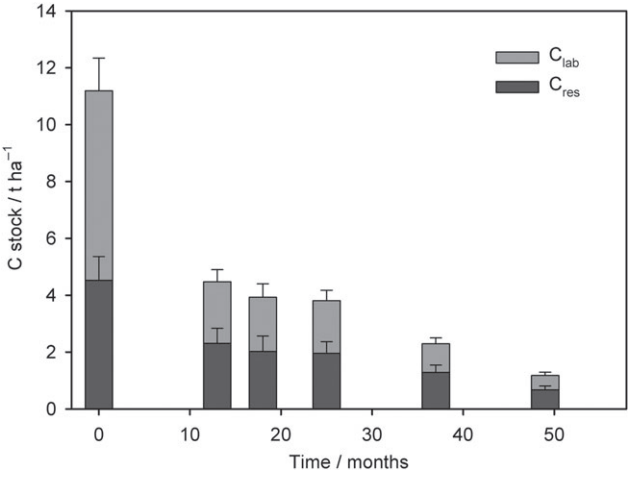

Figure 4 Stock of labile carbon pool (C_{lab}) and resistant carbon pool (C_{res}) of woody debris > 4 mm in the 0–30-cm layer. Values are means, error bars represent standard errors ($n = 14$ at the beginning of the experiment, $n = 18$ at the 13th and 18th months, $n = 72$ at the 25th, 37th and 49th months). See Table 3 for the calculation of variables.

4. The C_{lab} and C_{res} stocks decreased over time (Figure 4), but decomposition of C_{lab} was faster:

$$C_{lab} = 6.2 \times e^{-0.054t}, \quad (4)$$

$$C_{res} = 4.3 \times e^{-0.035t}, \quad (5)$$

where t is the time in months and carbon stocks are expressed in t ha^{-1}. The half-lives of C_{lab} and C_{res} were 12.9 and 19.9 months, respectively. Furthermore, the C_{lab}:C_{dc} ratio was 0.60 ± 0.01 in October 2008 and decreased to 0.50 after November 2009 (Table 4).

Discussion

Kinetics of woody debris mass loss

The first-order decay, describing the mass loss of woody debris (Figure 2), is commonly used to describe the decomposition of soil organic matter (Six & Jastrow, 2002). In Senegal (with a dry and sub-humid climate), Manlay *et al.* (2004) observed a greater rate of decay for woody roots buried in the soil, but in their study the roots were smaller (< 10 mm) than the woody debris in our study, especially in the first year after spreading the debris. Other research on the decomposition of dead wood in the Amazonian forest reported slower rates of decay than for our study, with a half-life of 4.1 years (Chambers *et al.*, 2000) and with a range of 2.3–14 years (excluding pioneer species, assumed to be absent in our work) (Hérault *et al.*, 2010). Our results showed that smaller debris buried in deforested soil had greater rates of decomposition, with a half-life of 17.6 months. Such a result might be expected because of the larger size of debris in the forest studies, which reduces the surface area for weathering and biological activities, especially microbial degradation. Furthermore, decomposition processes might be accelerated after deforestation because of the increase in soil temperature (Nascimento & Laurance, 2004).

At the experimental site, the annual soil temperature at 10-cm depth ranges from 24.7 to 26.0°C in the forest and from 24.6 to 32.6°C in cultivated plots (Petitjean, 2013). On the same date, the temperature difference between forest and cultivated plots can reach 8°C (Petitjean, 2013). Furthermore, on cultivated land solar radiation can reach the topsoil surface directly (Van Wambeke, 1992). This increase in temperature in cultivated soil could accelerate mineralization, although the effect of temperature above 30°C on mineralization remains unclear (Paul, 2001). Soil moisture conditions are also favourable to microbial and fungal activity because the soil is moist and never waterlogged. White-rot fungi were observed under the litter layer after deforestation, but termite activity was not observed. The large variation in decay patterns can be explained by the numerous species of trees before deforestation and by the spatial variation in the woody debris that was spread during deforestation. We found a wide range of C:N ratios in fresh woody debris (Table 4), which reflects tree diversity, the nature of wood and plant phonological stage. In the Paracou forest, within 10 km of our study site, Hérault *et al.* (2010) showed that variation in wood density was large, from 0.46 to 1.24 g cm^{-3} (again excluding pioneer species), and that rates of decay of dead wood depended on wood density. The mass loss of woody debris did not depend on the cropping system, but mainly on the general soil and climatic conditions because of the short time period studied and the large variation in the rate of decay of woody debris. Furthermore, the largest mass loss occurred during the first year after deforestation before the three crop systems were established in December 2009. During this first year the soil was under the same cover crops (Perrin *et al.*, 2014).

We found only one study in a similar climatic area where the mass of wood mulch was measured after deforestation and after the establishment of land for cropping. Davidson *et al.* (2008)

found that carbon stock from the litter layer in a 'chop-and-mulch' crop system was 17.7 ± 0.4 t ha^{-1} immediately after the input of woody mulch and 1.9 ± 0.3 t ha^{-1} after 34 months of cultivation, whereas we observed a decrease in carbon stock from woody debris of 11.2 ± 1.9 to 2.3 ± 0.4 t ha^{-1} after 37 months of cultivation. The rate of decomposition of woody mulch in the study by Davidson *et al.* (2008) appears to be faster than that in our study. However, Davidson *et al.* (2008) did not report the size of debris, and the soil of their site was not tilled after deforestation or before cultivation, whereas the converse was true for our study. The comparison of these two studies emphasizes the need for further research to test the effect of burying woody debris on its decay.

The decomposition of woody debris contributed to total soil organic carbon stock through a fragmentation process because the mass loss of woody debris was not completely converted into CO_2 by mineralization. On the same experimental site in November 2009 and April 2010 we observed more soil organic carbon in the soil fraction < 2 mm of cultivated plots than that of the forest (Perrin *et al.*, 2014). Figure 5 shows that a large part of the woody debris and other carbon inputs from deforestation (forest litter and coarse forest roots) were fragmented finely during their decomposition, which explains the increase in carbon in the soil fraction < 2 mm and in other plant debris > 2 mm up to 18 months after deforestation. Nevertheless, carbon that was freshly incorporated into the soil was probably mineralized rapidly because we observed a large decrease in soil carbon in the fraction < 2 mm between 18 and 25 months (April–October 2010) after deforestation (Perrin *et al.*, 2014). Further research is required to assess the proportion of carbon in soil that is lost as CO_2 or dissolved organic carbon, and the proportion of carbon incorporated into the soil.

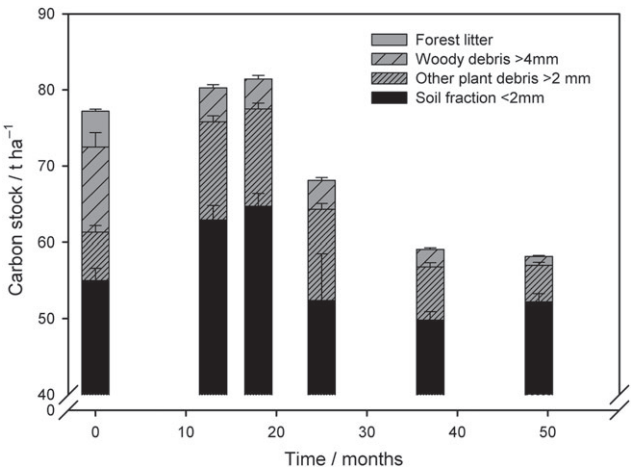

Figure 5 Carbon stocks in forest litter, woody debris > 4 mm, other plant debris > 2 mm and soil fraction < 2 mm at deforestation and in cultivated soil. Values are means, error bars represent standard errors ($n = 17$ at deforestation and $n = 72$ in cultivated soil for other plant debris > 2 mm and soil fraction < 2 mm), calculated from the data of Perrin *et al.* (2014).

Organic matter transformation during the decomposition of woody debris

The organic geochemistry of woody debris evolved quickly during its decomposition in soil, as attested by the decrease in the C:N ratio, Rock-Eval HI and R400, and OM-C_{lab} one year after deforestation. In parallel, OM-C_{res} increased during the first year of the experiment (Table 3). Decarboxylation, dehydrogenation and mineralization of labile components occurred after the spreading and burial of woody debris. A decrease in the C:N ratio during decomposition has been observed also for woody roots (Manlay *et al.*, 2004) and for woody debris (Mackensen & Bauhus, 2003; Olajuyigbe *et al.*, 2011).

With Rock-Eval pyrolysis, Disnar *et al.* (2003) observed that the hydrogen index (HI) decreased from top to bottom in the litter horizons. In other words, HI decreases as organic matter is transformed biochemically by biodegradation. The same process can explain the decrease in R400 after burial of woody debris; compounds such as hemicellulose, cellulose and slightly-oxidized lignin (fresh and labile organic matter) are pyrolysed mostly below 400°C, whereas complex and more stable organic matter is pyrolysed above 400°C (Disnar *et al.*, 2003). Therefore, R400 can be considered as an indicator of humification or organic matter transformation or stabilization, or both (Disnar *et al.*, 2008; Gogo *et al.*, 2011). In our case, R400 showed slight humification only of woody debris, mostly during the first year of the experiment. The oxygen index (OI) did not change in our experiment (Table 4), whereas we might have expected an increase related to oxygen enrichment during humification (Disnar *et al.*, 2003). Oxidation in our case did not play a major role in transformation of the wood. The oxygen index indicates either the oxygenated character of the organic matter according to its origin or is associated with the physico-chemical oxidation of organic matter over time. In the case of organic matter preservation OI decreases, but during humification OI generally increases because of oxidative alteration and polymerization. In our case the stability of OI and decrease in HI can be attributed to the humid tropical climate, which promotes the degradation of woody debris by fungi and bacteria with little humification.

The changes in C:N ratio and R400 show that decarboxyation, dehydrogenation and humification occurred mainly in the first year after the spreading of woody debris. The HI and OM-C_{lab}, however, continued to change after the first year of the experiment (Table 4), showing that decomposition of woody debris was progressive. Consequently, C_{lab} and C_{res} decreased with time, so there was neither long-term biochemical preservation nor polymerization of organic matter in the form of woody debris (Figure 4). This absence of organic matter preservation in woody debris and lack of humification over time accords with first-order decay for mass loss of woody debris. The decrease in the C_{lab}:C_{dc} ratio occurred during the first year only after deforestation (Table 4). The quantity of C_{res} represents the carbon pool that is initially resistant, but its decomposition with time might produce labile biochemical compounds that could be pyrolysed and identified as C_{lab}.

Rock-Eval pyrolysis as a tool to assess the fate of OM in soils

Rock-Eval Pyrolysis is a simple method that enables us to (i) assess the chemical transformation of woody debris during its decomposition and (ii) distinguish two carbon pools with different responses to decomposition. The changes in the organic geochemistry of plant residue determined by Rock-Eval pyrolysis were more gradual than those of the C:N ratio (Table 4). The relationship between R400 and the C:N ratio confirms the value of R400 for assessing the humification of fresh organic matter (Figure 6) during its decomposition. One year after deforestation (decomposed woody debris), R400 was correlated with C:N ($r = 0.61$, $P < 0.001$, $n = 30$). Fresh woody debris sampled in October 2008 showed a wide range of C:N ratios, but little variation in R400 (Figure 6). The wide range of C:N ratios can be explained by the large number of woody species that were shredded during deforestation and that have different nitrogen contents. However, nitrogen content does not affect the proportions of hemicellulose, cellulose and lignin compounds, which are pyrolysed mainly below 400°C and explain the lack of variation in R400 for woody debris in October 2008 ('fresh woody debris' in Figure 6).

The novelty of this study is that we did not focus on only HI, OI and R400. These properties are obtained from the pyrolysis stage and are the most discussed in soil organic matter studies (Disnar *et al.*, 2003; Sebag *et al.*, 2006; Carrie *et al.*, 2012). Other Rock-Eval properties, such as OM-C_{lab} and OM-C_{res}, also showed the transformation of woody debris. More attention should be given to the carbon released during oxidation and at the end of pyrolysis, which corresponds to the OM-C_{res} pool. We showed that this pool might represent more than 50% of the organic matter in woody debris one year after deforestation. Finally, use of Rock-Eval pyroloysis for the determination of carbon stocks in woody debris enabled the absolute amount of labile and resistant carbon and their half-lives, corresponding to the C_{lab} and C_{res} pools, to be monitored over time (Figure 6). The C_{lab} and C_{res} values highlight the lack of preservation and humification of organic matter in the woody debris. However, we could not link carbon pools that we determined in this study directly to classic organic compounds (soluble carbon, sugars, cellulose, lignins and waxes). Deconvolution of the S2 pyrogram can be used to discriminate between different organic constituents (Sebag *et al.*, 2006), but this approach might be limited for materials rich in cellulose and lignin. The latter have a similar maximum temperature to that of the S2 peak, and furthermore the lignin S2 peak is wide (Disnar *et al.*, 2003).

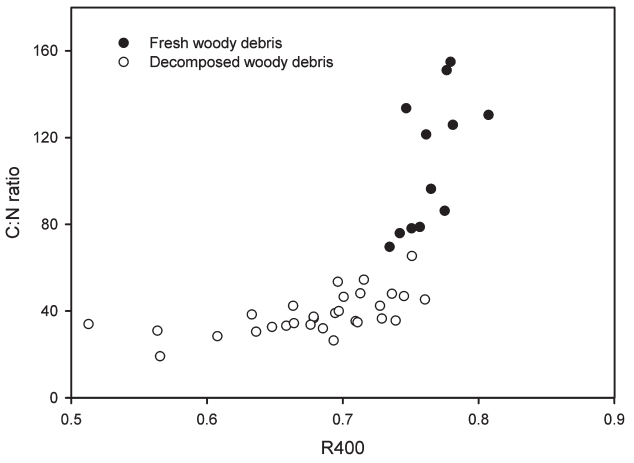

Figure 6 Scatter diagrams of C:N ratio against R400 (portion of the S2 signal below 400°C) for woody debris > 4 mm.

For studies of woody debris with Rock-Eval pyrolysis we suggest the following: (i) consider that the 'MinC' fraction is an organic fraction and group it with the RC fraction to form the C_{res} pool and (ii) measure organic matter content and C_{dc} (carbon content measured by dry combustion). This enables two carbon pools, C_{lab} and C_{res}, to be determined that respond to decomposition and humification, and whose evolution over time can be compared for a given amount of organic matter.

Conclusions

Decomposition of woody debris in a deforested and cultivated soil in a humid tropical climate was rapid, with a half-life of only 17.6 months, and was characterized by a first-order function. This decay is faster than that reported for coarser woody debris in forest ecosystems because of the smaller size of the debris and the hotter conditions in this study.

Rock-Eval pyrolysis enabled the overall organic geochemistry of the decomposition of woody debris to be studied, and it showed that it changed rapidly with time. After burial, woody debris was more thermally resistant and the proportion of labile carbon decreased. However, there was little humification and even the resistant carbon pool decreased during the 4 years of our study, in accord with first-order decay of the debris. Our study shows that the benefits of amending the soil with woody debris to create soil carbon occur only during the first year after deforestation because of its rapid decomposition.

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